

CATALYTIC DECOMPOSITION OF PALM OIL TO LIQUID FUELS AND CHEMICALS

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Abstract

An attempt was made to convert vapours of palm oil to liquid fuels and other chemicals by passing over various zeolite catalysts in a glass reactor. The catalysts used were in the zeolite family namely ultra-stable Y (USY), rare-earth Y (REY) and Na-Y. The liquid products were analyzed by gas chromatography. The results show that it is possible to alter the yield and compositions of the different hydrocarbon products by changing the reactor temperature, the type and amount of the catalyst. USY (6.0 g) at 425 °C, offered a liquid product (92.63 wt% of total liquid hydrocarbons) in the gasoline boiling range enriched with high content of aromatic hydrocarbons which turns out to be high-octane gasoline. Similar liquid product compositions were obtained by REY (6.0 g) at 425 °C with a liquid product of 95.49 wt% of total liquid hydrocarbons, in the gasoline boiling range in which 56.37 wt% of total liquid hydrocarbons, was contributed by benzene, toluene and xylenes alone, which have high octane ratings. Na-Y catalyst (6.0 g) produced ample amount of straight chain hydrocarbons (53.77 wt % of total liquid hydrocarbons) at 425 °C in the gasoline boiling range.

Introduction

The realization that non-renewable liquid fuels are going to be depleted and the price is going up, is the main reason why we are looking for the alternatives of non-renewable liquid fuels. Embargo set by the OPEC countries or war may create energy crisis to any country at any time, if the country is not self-sufficient in its own energy supply.

Thus, to combat that bad situation, researches are imperative to find out the alternatives of non-renewable liquid fuels. Economic considerations for the production of fuels may prove to be less important in the end than the assurance of the continuity of supply.

Vegetable oil, a nature's gift, is a good source of non-renewable hydrocarbons. Vegetable oils are triglycerides of long chain fatty acids (RCOOH) and glycerol, where relatively long chain CH₂ units of alkyl groups (-R) in fatty acids offer the source of hydrocarbons which can be realized as fuel by catalytic cracking. Weisz *et al.*, (1979) have created a new era in the field of catalytic cracking by upgrading high molecular weight biomass constituents to high quality fuels that could be gasoline substitute by using shape selective zeolite catalyst (HZSM-5). The commonly used catalyst for the conversion of vegetable oil to gasoline range hydrocarbons has been H-ZSM-5 (Weisz *et al.*, 1979; Prasad and Bakhshi, 1985; Prasad *et al.*, 1986). Recently Katikaneni *et al.*, (1995) have shown the conversion of vegetable oil over H-mordenite, H-Y, silicalite, alumina-pillared clay and silica-alumina.

For the catalytic cracking of vegetable oils to liquid fuels, very little attention has been given to ultra-stable Y (USY) and rare-earth exchanged Y (REY) zeolite which are known to be octane-enhancing catalysts in the crude oil refineries.

In this present work, we have converted palm oil to liquid hydrocarbons mostly in the gasoline boiling range and little in the kerosene and diesel boiling ranges and other aromatics using USY, REY and Na-Y zeolite catalysts. The effects of temperature and the amount of catalyst on the yields and composition of liquid hydrocarbons have been studied. A comparative study has also been carried out in order to see the effect of catalyst acidity on the liquid hydrocarbon yield and compositions using REY, USY and Na-Y zeolite as the catalyst.

Experimental

Feed Materials

Commercial palm oil (Brand: BURUH) was used in this study. The composition of Palm oil is given in Table 1.

Table 1: Fatty acid composition of palm oil

Fatty acid	Carbon no.	% Wt
Oleic acid	18:1	42.5
Palmitic acid	16:0	40.0
Linoleic acid	18:2	11.2
Lauric acid & others	-----	6.3

Source: PORIM Technical Advisory Service Unit .

Catalysts

Ultra-stable Y (USY), rare-earth Y (REY) and Na-Y zeolites were used in this study. The physical properties of these zeolites are given in Table 2.

Table 2: Some physical properties of zeolites.

Zeolite	SiO ₂ / Al ₂ O ₃ mole ratio	Pore size, Å	Acid sites, moles of NH ₃ / Kg Catalyst	Surface area, BET (m ² / g)
USY	5.8	8	1.140	600
REY	4.8	7.4	1.196	600
Na-Y	5.6	8	0.768	700

Experimental set-up

A very simple glass apparatus was used in this experiment. It consists of a three-necked round bottom heating flask, one glass tube reactor coupled with heating tapes and temperature controller, and one condensation unit.

Procedure

Vapours of palm oil, generated by heating the flask at around 290°C - 300 °C, were passed over a fixed bed of catalyst and finally condensed to get the liquid product. The amount of catalyst was varied from 4g - 8g while the temperature was varied from 375 °C - 525 °C. The catalyst was preheated in presence of nitrogen for about 2 hours at the operating temperature. After completion of the experiment, the catalyst was heated at 500 °C in order to get rid of coke. The difference in weight before and after heating at 500 °C, was termed as coke.

Product analysis

The liquid products were analyzed by gas chromatography. The identity of the chromatographic peaks were determined by using pure compounds and by GC-MS. The liquid products were also analyzed by FTIR in order to check any fatty acid or ester group.

Results and Discussion

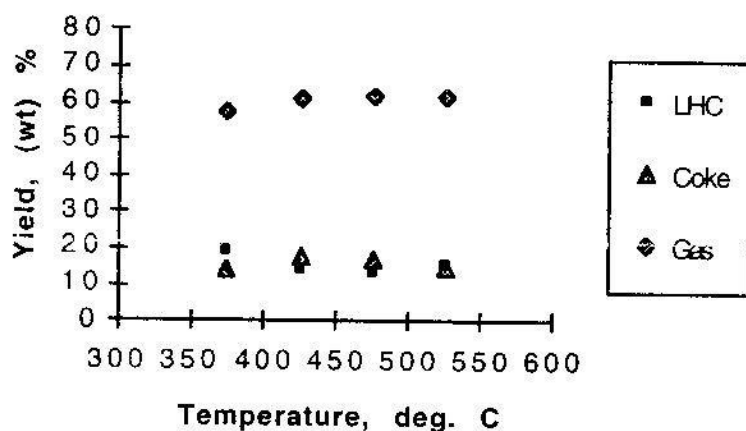
The products obtained from the cracking of palm oil using USY, REY and NaY can be grouped into gaseous hydrocarbons (C₁-C₅), oxides of carbon (CO and CO₂), liquid hydrocarbons (C₆-C₂₀), water and coke. The liquid hydrocarbons (C₆-C₂₀), were found mostly in the gasoline (C₆-C₁₁) boiling range and little in the kerosene (C₁₁-C₁₅) and diesel (C₁₅-C₂₀) boiling ranges.

Two possible routes are proposed for the conversion of bulky triglyceride molecules of vegetable oil into smaller hydrocarbons (Katikaneni *et al.*, 1995). One possible route is that initial cracking occurs on the external surface of the catalyst and produces smaller intermediate molecules which enter into the pores of the catalyst where secondary internal cracking takes place and produces light olefins. Further these light olefins give paraffinic and aromatic hydrocarbons by polymerization and aromatization reactions into the zeolite pores (Costa *et al.*, 1992). Another possibility is that the triglyceride molecules can penetrate into the zeolite pores and are cracked as proposed by Weisz *et al.*, (1979).

Effect of process variables

In order to investigate the effect of temperature and the amount of catalyst on the reaction products distribution, experiments were carried out between 375-525 °C with the varying of the catalyst from 4.0g - 8.0 g.

Fig.1 shows that as the temperature was raised from 375 °C - 525 °C, using USY (6.0 g) catalyst, the yield of liquid hydrocarbons gradually decreased and then showed a slight increment at 525 °C. This is very similar with the results of other researchers (Katikaneni *et al.*, 1995). This can be explained from the fact that with the rising of temperature and the amount of catalyst, the secondary cracking enhances to produce lighter hydrocarbon gases at the expense of liquid hydrocarbons. The gaseous olefins thus produced form aromatic hydrocarbons by aromatization reactions. More coke is produced as the polymerization reaction is likely to proceed with the rising of temperature and the amount of catalyst.



$$\text{Yield (wt\%)} = \frac{\text{wt. of a specific product}}{\text{wt. of converted material}} \times 100$$

Figure 1. The effect of temperature on the yields of liquid hydrocarbons (LHC), coke and gas.

It can be seen from Fig.2 that as the amount of catalyst (USY) increased, the liquid hydrocarbon yield decreased while the gases and coke showed an increasing trend.

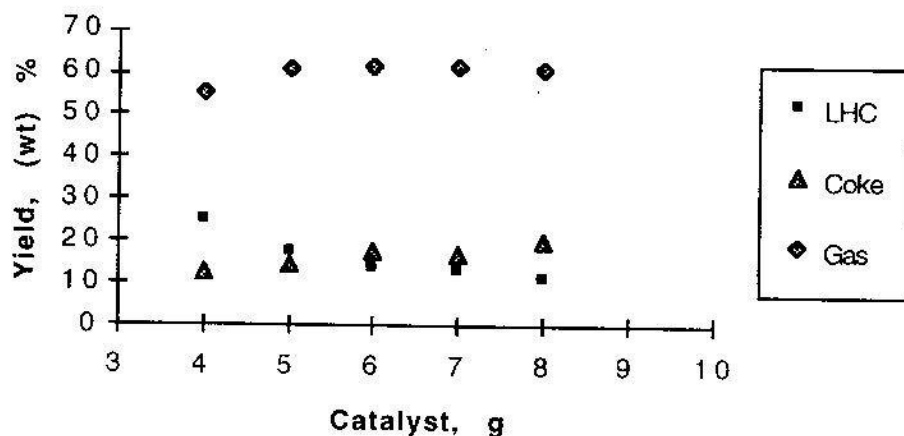


Figure 2. The effect of the amount of catalyst on the yields of liquid hydrocarbons (LHC), coke and gas.

Liquid hydrocarbon product compositions

The compositions of liquid hydrocarbon products are presented in Table 3. It can be observed that ample amount of iso-paraffins and aromatics like benzene, toluene, xylenes and other alkylated aromatics which have high octane ratings and thus are highly desirable in high octane gasoline were obtained by using USY catalyst in every cases. A gasoline yield of 92.63 wt% of the liquid hydrocarbons was obtained by USY (6.0 g) at 425 °C (Table 3). Toluene and xylenes which are important organic chemicals were obtained as high as 29.60 wt% and 18.40 wt% of the total liquid hydrocarbons, respectively, by using USY (6.0 g) at 425 °C (Table 3).

Table 3. Liquid hydrocarbon product compositions (wt %) for different amounts of USY at 425 °C.

Components,	Wt %				
	4.0	Amount 5.0	of 6.0	catalyst, g 7.0	8.0
C6-C11 (n-Paraffins)	9.79	12.98	10.0	27.10	9.71
C6-C11 (iso-Paraffins + Olefins + Aromatics)	39.24	48.69	25.83	26.45	15.63
C12-C15 (n-Paraffins)	11.89	6.50	1.85	11.26	15.96
C12-C15 (iso-Paraffins + Olefins + Aromatics)	10.24	8.79	3.59	8.64	5.93
C15+ (Aliphatics + Aromatics)	5.25	2.47	1.93	4.6	8.20
Benzene	3.36	2.97	8.80	11.5	6.93
Toluene	10.98	10.27	29.60	4.04	23.22
Xylenes	9.25	7.33	18.40	6.41	14.42

One experiment was carried out at 425 °C, where three different catalysts namely USY, REY and Na-Y, all having different acidity were used in order to study the effect of acidity on cracking.

Table 4. Yields obtained at 425 °C using USY, REY and Na-Y catalysts.

Catalyst	Acid sites, NH ₃ moles / Kg catalyst	Liquid Hydrocarbons, Wt%	Water, Wt%	Coke, Wt%	Gas, Wt%
REY	1.196	11.69	9.06	22.17	57.08
USY	1.140	13.82	7.02	17.78	61.38
Na-Y	0.768	20.93	6.02	12.85	60.20

It was found that Na-Y having the lowest acidity among all the three catalysts, produced much higher amount of liquid hydrocarbons than USY and REY produced (Table 4) which suggests that the acidity in USY and REY plays the vital role in cracking where liquid hydrocarbons are further cracked to form gaseous hydrocarbons which undergo a number of aromatization reactions namely, cyclization, H-transfer and isomerization to produce aromatic hydrocarbons. These aromatic hydrocarbons are responsible for generating coke by ploycondensation. The formation of aromatic hydrocarbons from olefins is well demonstrated by Chantal *et al.*, (1984). Na-Y offered the highest amount of n-paraffins (53.77 wt% of the liquid hydrocarbons) in the gasoline boiling range while it produced little amount of benzene, toluene and xylenes (Table 5) which suggests that the rates of cracking were higher than the rates of cyclization and H-transfer reaction.

Table 5. Liquid hydrocarbon product compositions (wt %) for different catalysts at 425°C.

Components,	Wt %		
	USY (6.0 g)	REY (6.0 g)	Na-Y (6.0 g)
C6-C11 (n-Paraffins)	10.0	7.61	53.77
C6-C11 (iso-Paraffins + Olefins + Aromatics)	25.83	31.56	31.05
C12-C15 (n-Paraffins)	1.85	1.48	1.87
C12-C15 (iso-Paraffins + Olefins + Aromatics)	3.59	1.50	2.02
C15+ (Aliphatics + Aromatics)	1.93	1.53	1.0
Benzene	8.80	8.27	1.87
Toluene	29.60	28.45	4.24
Xylenes	18.40	19.60	4.18

Aromatics and isomeric hydrocarbons are known to enhance the octane value of the fuel. Figure 3 shows that at 425 °C, Na-Y (6.0 g) offered aromatics and isomeric hydrocarbons of 41.43 wt% of the total liquid hydrocarbons, in the gasoline boiling range, which contribute little octane value to the fuel. On the other hand, REY (6.0 g) and USY (6.0 g) offered aromatics and isomeric hydrocarbons of 87.88 wt% and 82.63 wt% of the total liquid hydrocarbons, respectively, in the gasoline boiling range (C6-C11) which impart high octane value to the fuel.

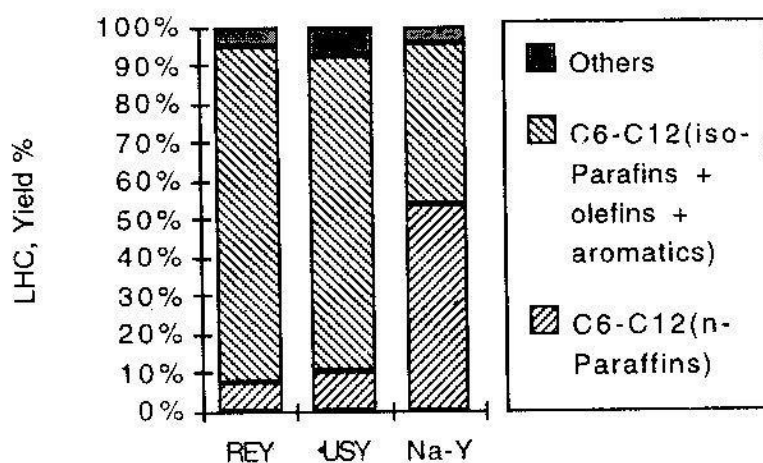


Figure 3. The production of gasoline boiling range hydrocarbons by REY, USY and Na-Y catalysts.

Conclusion

From this research it can be concluded that

1. Palm oil showed the feasibility to be converted to liquid hydrocarbons in the gasoline (C₆-C₁₁), kerosene (C₁₂-C₁₅), and diesel (C₁₅-C₂₀) boiling ranges and other important organic chemicals like benzene, toluene and xylenes by using Ultra-stable Y (USY), rare-earth Y (REY) and Na-Y zeolites.
2. The catalyst USY (6.0 g) offered a product of 92.63 wt% of the total liquid hydrocarbons, in the gasoline boiling range (C₆-C₁₁) at 425 °C in which 56.8 wt% of the total liquid hydrocarbons was contributed by benzene, toluene and xylenes alone which in turn contribute in raising the octane numbers.
3. The parameter study for USY suggests that with the rising of the temperature and the amount of catalyst, the liquid product decreased while aromatics and coke content increased.
4. In a comparative experiment, it was observed that at 425 °C, REY (6.0 g) and USY (6.0 g) offered liquid products of 95.49 wt% and 92.63 wt% of total liquid hydrocarbons, respectively, in the gasoline boiling range (C₆-C₁₁) enriched with high aromatic content which turned out to be high-octane gasoline, while Na-Y (6.0 g) offered a liquid product of 95.11 wt% of total liquid hydrocarbons, in the gasoline boiling range with ample amount of straight chain hydrocarbons which contributes low octane value to the fuel.
5. Na-Y, having low in acidity, produced linear chain hydrocarbons as high as 53.77 wt% of total liquid hydrocarbons while produced little amount of aromatic hydrocarbons like benzene, toluene and xylenes.

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